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(54) POLYAMIDE COMPOSITIONS WITH IMPROVED HEAT STABILITY

(71) We, RHONE-POULENC INDUSTRIES, a French Body Corporate of, 22 Avenue Montaigne, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polyamide compositions with improved heat stability.

Very many heat-stabilised polyamide compositions are known. Amongst the stabilisers used there may be mentioned mixtures of potassium iodide and a copper complex (see, for example, Russian Patent No. 352,917 or British Patent Specification No. 1,192,756) and mixtures of alkali metal halides or alkaline earth metal halides and organic salts of copper (see, for example, British Patent Specification No. 1,368,776).

The stabilisers already known, however, suffer from various disadvantages. For example, a pronounced colouration of the polyamide composition occurs or there is insufficient stabilising activity. Accordingly there has been a need to find a stabiliser system which has very good activity but which does not impart a colouration to the compositions into which it is incorporated. In fact, it is important to have available colourless or very slightly coloured compositions which make it possible to obtain either colourless or white articles, or articles in pure colours (by adding selected dyestuffs or pigments) without the basic shade being modified or adversely affected by undesired subsidiary colourations.

According to the present invention, there are provided polyamide compositions of improved heat stability and exhibiting little colouration which contain, relative to the weight of the polyamide:

- (a) from 0.04 to 3%, preferably from 0.08 to 2%, by weight of an alkali metal halide or alkaline earth metal halide,
 (b) an organic or inorganic, complexed or

non-complexed, copper salt in an amount such that from 0.001 to 2%, preferably from 0.005 to 0.5%, by weight of copper is present, and

(c) from 0.1 to 5%, preferably from 0.2 to 1.5%, by weight of a glycol which has from 3 to 20 carbon atoms, the hydroxyl groups of which are located in the α - and γ -positions on the hydrocarbon chain.

By "polyamides" there are understood the products obtained by polycondensation of diamines with dicarboxylic acids or by polymerisation of aminoacids. The most common polyamides are the polyhexamethyleneadipamides, the polyhexamethylene-sebacamides, the polyhexamethylene-azelamides, the polyhexamethylenedodecanediamides, the polydodecamethyleneoxamides, the polyaminocaprolactams, the polyundecanamides, the polylaurylactams, as well as the corresponding copolymers.

Obviously the compositions according to the invention, intended especially for the production of shaped articles, can contain reinforcing or non-reinforcing fillers, in particular mineral fibres such as glass fibres or asbestos fibres, glass microspheres, talc, silica and micas.

Equally, various other adjuvants can be incorporated, such as lubricants intended to facilitate the use of the compositions, various types of stabiliser, reinforcing agents to increase the impact strength, plasticisers, pigments or dyestuffs, antistatic agents and crystallisation agents.

Amongst the alkali metal halides or alkaline earth metal halides, it is preferred to use the alkali metal salts or alkaline earth metal salts of hydriodic acid and hydrobromic acid, the most frequently used being the salts of sodium, potassium, calcium and magnesium. The use of potassium iodide is particularly advantageous.

The copper salts are usually salts derived from inorganic acids, more particularly halogen-containing acids, or derived from

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organic acids preferably having 1 to 24 carbon atoms, as well as from the complexed forms of such salts. Very suitable are cuprous and cupric halides, cupric acetate, cupric stearate and cupric acrylate. It is particularly advantageous to use copper stearate and cuprous iodide.

As glycols which can be used in the compositions of this invention there may be mentioned, in particular, 2,2-dimethyl-1,3-propanediol and 2-ethyl-1,3-hexanediol.

The three types of stabilising compounds used in this invention can be added before or after polymerisation of the polyamide. If the stabilisers are incorporated before polymerisation, the latter can be carried out either continuously or in separate operations in known manner, without a change in the colour of the molten polyamide being observed.

The stabilisers can also be incorporated into the polyamide or into the composition, either separately or together, by any known means; thus, for example, mixers, malaxators or extruders can be used.

It is possible to prepare a mixture of the three constituents and then to incorporate this mixture into the polyamide composition in solid or molten form. It is also possible to add the stabilisers, for example, in the feed hopper of an extruder. Provided homogenisation of the various components of the composition is good, the way in which they are incorporated does not affect the results.

The following Examples further illustrate the present invention.

EXAMPLE 1

480.6 g. of 2,2-dimethyl-1,3-propanediol are introduced into a 2-litre beaker provided with a cover, the beaker being placed in a bath thermostatically controlled at 150°C., and equipped with a turbine-type stirrer rotating at 400 revolutions per minute. The compound is allowed to melt for about 45 minutes and 125 g. of copper stearate are then added whilst stirring. After 2 minutes, 235.5 g. of potassium iodide of particle size less than 100 μ are introduced. Stirring is continued for about 15 minutes and it is found that the colour of the mixture, which originally was greenish-brown, changes to a very light beige which is almost white. The mixture of stabilisers is now poured onto a polyethylene terephthalate film and is allowed to cool; the mass obtained is then ground to give flakes of particle size less than 6 mm.

The stabiliser obtained above is mixed, and homogenised, with 60 kg. of polyhexamethylenedipamide having a viscosity index of 135 cm²/g. measured as a 0.5% solution in 90% formic acid in accordance with Standard Specification NF T 51,019.

This stabilised composition is placed in the hopper of a single-screw extruder having screw diameter (D) of 63.5 mm and a length of 24 D, and having an output of 45 kg./hour; the temperature of the barrel of the extruder is between 260° and 280°C. A ribbon is extruded and after cooling is chopped on a granulator.

Small plates of size 70×70×2 mm are injection-moulded on a screw injection moulding machine heated to between 280° and 285°C.

The small plates thus obtained are examined in comparison with other small plates prepared under the same conditions using a composition which does not contain glycol, in accordance with Standard Specification ASTM E 308-66 (Standard Recommended Practice for Spectrophotometry and Description of Colour on CIE 1931 System).

In this way, a luminosity Y, a purity index P and a colourimetric difference E between the two formulations, indicated in FMC II MacAdam units, are determined.

The results are as follows:

	Reference	Formulation containing glycol
Y	48.5%	53.5%
P	78.8%	85.0%
E		21.9

The heat stability of the composition is also evaluated. For this purpose, small plates, injection-moulded on a screw injection moulding machine heated to between 270 and 280°C., are prepared, the mould being heated to 80°C. These samples of size 6.35×3.17 mm are in accordance with type II of the ASTM Specification.

These small plates are placed in a ventilated oven, heated to 180°C., for varying periods.

The heat stability is determined by measuring the life which corresponds to the loss of 50% of the initial value of the tensile strength. This test is identical to that practised by the "Underwriters Laboratories" (UL) for the determination of the stability index.

In the aging test at 180°C., a life of 40 days was found for the composition containing the glycol. A comparison sample without glycol has a life of 34 days under the same conditions.

EXAMPLE 2

The procedure followed is as indicated in Example 1, with the following products in the following quantities, as stabilisers: 240.3 g. of 2,2-dimethyl-1,3-propanediol, 37.8 g. of cuprous iodide and 202.8 g. of potassium iodide.

The colourimetric properties are measured in accordance with the tests described in Example 1.

The following results are obtained:

	Reference	Formulation containing glycol
Y	58.8%	63%
P	85.8%	87.4%
E		7.3

EXAMPLE 3

The procedure followed is as indicated in Example 1, with the following products, in the following quantities, as stabilisers: 360 g. of 2-ethyl-1,3-hexanediol, 125 g. of copper stearate and 235.5 g. of potassium iodide.

The heat stability is measured in accordance with the UL tests described in Example 1. A life of 42 days was found in the aging test at 180°C. A reference sample without glycol has a life of 34 days under the same conditions.

WHAT WE CLAIM IS:—

1. A composition which comprises a polyamide and, relative to the weight of the polyamide:

(a) from 0.04 to 3% by weight of an alkali metal or alkaline earth metal halide,

(b) an organic or inorganic, complexed or non-complexed, copper salt in an amount such that from 0.001 to 2% by weight of copper is present, and

(c) from 0.1 to 5% by weight of a glycol possessing from 3 to 20 carbon atoms, the hydroxyl groups of which are located in the α - and γ -positions on the hydrocarbon chain.

2. A composition according to claim 1 which contains, relative to the weight of the polyamide, from 0.08 to 2% by weight of alkali metal or alkaline earth metal halide.

3. A composition according to claim 1 or 2 which contains, relative to the weight of the polyamide organic or inorganic, com-

plexed or non-complexed, copper salt in an amount such that from 0.005 to 0.5% by weight of copper is present.

4. A composition according to any one of claims 1 to 3 which contains, relative to the weight of the polyamide, from 0.2 to 1.5% by weight of said glycol.

5. A composition according to any one of claims 1 to 4 in which the glycol is 2,2-dimethyl-1,3-propanediol.

6. A composition according to any one of claims 1 to 4 in which the glycol is 2-ethyl-1,3-hexanediol.

7. A composition according to any one of claims 1 to 6 in which the alkali metal halide is potassium iodide.

8. A composition according to any one of claims 1 to 7 in which the copper salt is copper stearate.

9. A composition according to any one of claims 1 to 7 in which the cuprous salt is copper iodide.

10. A composition according to any one of claims 1 to 9 which also contains reinforcing or non-reinforcing filler.

11. A composition according to claim 10 which contains glass fibres, asbestos fibres, glass microspheres, talc, silica or mica.

12. A composition according to claim 1 substantially as hereinbefore described.

13. A composition according to claim 1 substantially as described in any one of Examples 1 to 3.

14. A process for preparing a composition as claimed in any one of the preceding claims which comprises mixing the halide, copper salt and glycol in the specified amounts either with the polyamide, or with the reactants for the polyamide and then polymerising the composition.

15. A process according to claim 14 substantially as herein before described.

16. A composition as defined in claim 1 whenever prepared by a process as claimed in claim 14 or 15.

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